

REACTION OF ACID GASES WITH SOLID ALKALI FLOWING IN A DUCT:
SO₂ REACTION WITH LIME

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ABSTRACT

Many new flue gas desulfurization processes are being developed where an acid gas and alkali are reacted cocurrently in a duct. Solutions to the material balance equations for cocurrent flow processes have been solved for the cases when the conversion is limited by gas phase diffusion, reaction kinetics, or diffusion thru the product layer. The solutions are presented in a graphical form and can be used to determine the residence time required to achieve a specified conversion of the gaseous component providing the appropriate rate constant is known. The curves can also be used to determine a rate controlling step from conversion versus time data taken in an isothermal flow reactor. This method is applied to the application of the high temperature reaction of lime with SO₂ for conditions that would occur in the duct downstream of a direct coal fired heat engine combustor.

INTRODUCTION

Low capital cost flue gas desulfurization processes are being developed to address the potential market for retrofit systems on existing boilers burning medium to high sulfur coal. Many of these new systems involve the injection of a dry solid of calcium or sodium alkali in the duct to react with the SO₂ in the flue gas. Calcium alkali tend to be the preferred reagents compared to those of sodium because of the availability and lower cost.

The stoichiometry ratio of moles of calcium fed to the moles of SO₂ is often in the range of 2 to 3 for the in-duct processes. Attempts to improve the utilization of reagent have stressed the need for small particles of high BET surface area and porosity. Calcium hydroxide, commercially produced, with those properties has achieved the highest utilizations compared to other calcium alkali.

Injection processes may also be feasible for removing SO₂ from flue gas produced by a direct coal fired heat engine combustor. In this application the gas is expected to be at a high temperature and pressure. This paper presents estimates of the reaction time required for a variety of operating conditions where the reagent is calcium hydroxide.

PREVIOUS WORK

Borgwardt, et al.(2) have shown that the utilization of calcium oxide particles with a BET surface area of 32 m²/g reacting with COS at 5000 ppm at 700°C is independent over a particle size range of 1 to 9.4 microns. They concluded that the reaction occurs equally throughout the particle and that pore diffusion resistance must be insignificant.

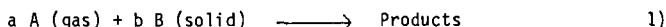
In a later study Borgwardt and Bruce (1) measured the conversion of 1 micron calcium oxide particles by reaction with SO₂ at a concentration of 3000 ppm in a differential reactor over a temperature range of 760 to 1125°C. The primary

resistance to SO_2 absorption was ionic diffusion thru the product layer. A conventional grain model accurately correlated the data when the concentration of the diffusing ion was computed to be proportional to the gas concentration to the 0.62 power.

Bortz, et al.(3) has studied the reaction of small particles of calcium hydroxide at temperatures of 450 to 600°C which are typical of economizers on utility boilers. These tests were done in an isothermal flow reactor. With particles in the range of 1 to 5 microns with BET surface areas greater than 20 m^2/gm , the absorption of SO_2 was dependent on the gas phase mass transfer rates of SO_2 relative to the kinetic rate of CO_2 with the hydroxide. Pore diffusion resistance was negligible.

THEORY

A generalized reaction of a single gas A reacting irreversible with solid B is given by Equation 1 where a and b are the stoichiometric coefficients.



When the reaction rate is controlled by diffusion of the gaseous reactant thru the inert layer of product formed over the unreacted core of solid reagent, the radius of the unreacted core, r, at any time is given by (4):

$$-\rho \frac{r^2 dr}{M} \left(\frac{1}{r} - \frac{1}{R} \right) = D_d C_A (b/a) dt \quad 2)$$

Following the approach used by Borgwardt and Bruce (1) the initial grain radius of the solid, R, is related to the BET area by:

$$R = 3/(S_a \rho) = 3/(10^4 S_g \rho) \quad 3)$$

By expressing the moles of solid reactant remaining at any time per mole of gas reactant at the inlet to the fraction of reactant A remaining the partial pressure of reactant A can be expressed as:

$$P_A = P_{Ain} \left[\frac{F_a}{b} \left(\frac{r}{R} \right)^3 + 1 - \frac{F_a}{b} \right] = P_{Ain} \left[S \left(\frac{r}{R} \right)^3 + 1 - S \right] \quad 4)$$

where F is the moles of solid reactant B fed/moles of gas reactant A.

The fraction removal efficiency is related to the partial pressure of reactant A by:

$$1-E = P_A/P_{Ain} \quad 5)$$

Combining Equations 4 and 5 gives the grain radius at any time in terms of the fractional removal efficiency:

$$(r/R) = \left[1 - (E/S) \right]^{1/3} \quad 6)$$

The concentration term C_A in Equation 2 is that of the specie that diffuses thru the product layer. Borgwardt and Bruce (1) expressed the concentration in terms of the partial pressure of the gas as:

$$C_A = k_o P_A^m \quad 7)$$

Substitution of Equation 4 into Equation 7, and then substitution of the result into Equation 1 and integrating from the initial condition r/R equal 1.0 at time zero gives:

$$I_d = \int_1^{xf} \frac{(x^2 - x)dx}{[Sx^3 + 1-S]^m} = k_g dt \quad (8)$$

where x is set equal to r/R and k_d is the lumped constant:

$$k_d = (k_o D_d M b) / (\rho R^2 a) p_{Ain}^m = 10^8 k_o D_d M S g^2 \rho (b/a) p_{Ain}^m / 9 \quad (9)$$

Assuming m is fixed the value of the integral is determined for any specified feed ratio and final fractional conversion efficiency. The upper limit on the integral is found from Equation 6. Analytical solutions for the integral for all real value of m when S equals 1.0 and for all values of S when m equals 1.0 are listed in Table 1.

When the conversion of reactant A is controlled by a first order reaction with respect to A at the surface of the unreacted core, the radius of the unreacted core is given by (4):

$$-\frac{\rho}{M} \frac{dr}{dt} = k_r C_A (b/a) \quad (10)$$

By utilizing Equations 3 to 7 in an analogous manner, with m set equal to 1.0 the Equation 10 can be expressed as:

$$I_c = - \int_1^{xf} \frac{dx}{Sx^3 + 1-S} = k_r dt \quad (11)$$

where k_c is:

$$k_c = 10^4 k_r k_o M S g (b/a) p_{Ain} / 3 \quad (12)$$

The analytical solution of the integral in Equation 11 is given in Table 1.

If the conversion of reactant A is controlled by diffusion from the bulk gas to the outer surface of the grain, the radius of the unreacted core is given by (4):

$$\frac{\rho}{M} \left(\frac{r}{R} \right)^2 \frac{dr}{dt} = k_g C_A (b/a) \quad (13)$$

With m equal to 1.0, Equation 13 can be expressed as:

$$I_g = - \int_1^{xf} \frac{x^2 dx}{Sx^3 + 1-S} = k_g dt \quad (14)$$

where k_g is:

$$k_g = 10^4 k_g k_o p_{Ain} M (b/a) S g / 3 \quad (15)$$

The analytical solution of the integral is given in Table 1.

The values of the integrals given by Equations 8 for $m=1$ and Equations 11 and 14 are plotted on Figures 1, 2, and 3, respectively. These relationships do not account for expansion or contraction of the outer radius of the grain from the differences in the molar volumes of the reactant and product.

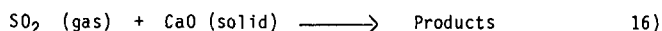
APPLICATION OF THE GRAPHICAL SOLUTIONS

With conversion versus time data taken in a flow reactor the graphical solutions provide a rapid method of determining if the conversion is controlled by one of the three assumed mechanisms. For the known value of S and measured value of E , a value of I is read from each curve and divided by the residence time to get values for the constants k_d , k_c , and k_g . This process is repeated for each set of data taken. If the lumped parameter for any one of the mechanisms is constant then that mechanism is applicable to the process. If some test runs used different initial gas concentrations that effect can be isolated from the computed constants.

For a known reaction system where one of the three assumed mechanisms is applicable and if the rate constant is also known then the graphical solution can be used to compute the residence time in a flow reactor. For example, assume a reaction is controlled by diffusion of the gas thru the product layer, so that m is 1.0, the BET area is known, and the diffusion coefficient had been determined from a data on a differential reactor. The lumped parameter k_d can be computed from Equation 9. Figure 1 would then be used to read a value of the integral for any values of S and E selected. The required residence time can be easily computed for each case by dividing the value of the integral by the lumped constant.

SO₂ REACTION WITH LIME AT HIGH TEMPERATURE

If calcium hydroxide is injected into a hot flue gas where the temperature exceeds 700°C dehydration of the particle occurs very rapidly. The calcium oxide that forms is a small particle with about 50 % porosity and a high surface area. For this application the grain model should be applicable. The reaction of the SO₂ with the lime at these conditions produces calcium sulfate, and can be expressed as:



For this reaction a and b are both 1.0.

One such commercial application may be in the removal of SO₂ from the combustion gas from a direct coal fired turbine operating at temperatures in the range of 950 to 1200°C at pressures of 1013 to 1520 kPa (10 to 15 atm). By removing the SO₂ at the high pressure the volume of the gas being treated is much less than downstream of the turbine. The feasibility of using calcium hydroxide injection upstream of the turbine to remove the SO₂ depends on the reaction time required.

The data of Borgwardt and Bruce (1) can be used in conjunction with Equation 8 to estimate the residence time. They concluded the conversion of lime at these temperatures is controlled by ionic diffusion thru the product layer, where m is 0.62 and the diffusion coefficient in Equation 9 is expressed as:

$$D_d = D_o * \exp(-E'/RT) \quad 17)$$

where E' in Equation 17 is the activation energy of 36,600 kcal/mol and T is the temperature in °K. Substitution of Equation 17 into Equation 9 yields:

$$k_d = (10^8 M k_o D_o / 9) (S_g^2 P_{SO_2 in}^{-.62} \exp(-E'/RT)) \quad 18)$$

Borgwardt and Bruce correlated k_d by:

$$k_d = (10^8 M k_o D_o / 9) (6 S_g^2 P_{SO_2 in}^{-.62}) * \exp(-E'/RT) = 2.65 S_g^2 P_{SO_2 in}^{-.62} \exp(-E'/RT) \quad 19)$$

Equating the second and third terms in Equation 19 gives:

$$10^8 * M * k_0 * D_0 * / 9 = 2.65/6 = 0.4417 \quad 20)$$

Equation 18 can now be written as:

$$k_d = 0.442 * S_g^2 P_{SO_2 in}^{.62} * \exp(-36,600/RT) \quad 21)$$

Since m equals 0.62, Equation 8 must be solved numerically except when S equals 1.0. The values for the integral are given in Figure 4. To compute the conversion time, the temperature, feed ratio, inlet SO_2 concentration and operating pressure must be specified. The inlet partial pressure of SO_2 is then computed and Equation 19 is used to compute k_d . For the specified fractional removal efficiency a value of I_d is read from Figure 4 and divided by k_d to obtain the reaction time. Table 2 summarizes calculations for the reaction time when the operating pressure is set at 1520 kPa (15 atm). At the higher temperature a lower BET area was assumed to account for sintering.

CONCLUSIONS

For dry injection FGD processes utilizing small particles of calcium hydroxide or calcium oxide a grain model can be used to represent the reagent utilization.

The reaction time required for the high temperature, high pressure conversion of SO_2 with small lime particles can be predicted with a modified grain model that accounts for the changing SO_2 partial pressure when the rate controlling step is diffusion thru the product layer.

NOMENCLATURE

A	- gaseous reactant
a	- stoichiometric coefficient for gas A
B	- solid reactant
b	- stoichiometric coefficient for solid reactant B
C	- concentration of diffusing specie, gmol/cm
D _d	- diffusion coefficient in product layer, cm /sec
D ₀	- Arrhenius pre-exponential factor
E	- fraction conversion efficiency of gaseous reactant
E'	- apparent activation energy taken as 36,600 cal/gmol
F	- moles of reactant solid fed/mole of gas reactant fed
I _C	- integral defined by Equation 11
I _d	- integral defined by Equation 8
I _g	- integral defined by Equation 14
k	- $((1-S)/S)^{1/3}$
k _C	- constant defined by Equation 12
k _d	- constant defined by Equation 9
k _g	- constant defined by Equation 15
k _G	- gas phase coefficient in Equation 13, cm/sec
k ₀	- constant defined by Equation 7
k _r	- reaction rate constant in Equation 10, cm/sec
M	- molecular weight of reactant solid
m	- constant defined by Equation 7
P _A	- partial pressure of gas A, Pa
P _{Ain}	- partial pressure of gas A at inlet conditions, Pa
P _{SO₂}	- partial pressure of SO ₂ , Pa
P _{SO₂in}	- partial pressure of SO ₂ at inlet conditions, Pa
R	- initial grain radius defined by Equation 3, cm; the gas constant in Equations 17, 18, 19 and 20, 1.987 cal/gmol- K
S	- Fa/b
S _a	- BET area of solid, cm ² /g
S _g	- BET area of solid, m ² /g
T	- temperature, °K
t	- time, sec
x	- r/R where R is the initial grain radius
x _f	- r/R at the end of the reaction time
∫	- mass per unit volume of grain, g/cm ³

LITERATURE CITED

1. Borgwardt, R.H., and Bruce, K.R., AIChEJ. 1986 32, 239.
2. Borgwardt, R.H., Roache, N.R., and Bruce, K.R., Environ. Prog. 1984a, 3, 129.
3. Bortz, S., Roman V. P., Yang, R. J., and Offen, G. R., EPA/EPRI Dry SO₂ and Simultaneous SO₂/NO_x Control Technology, 1986, Paper 6C, Raleigh, NC.
4. Levenspiel, O. "Chemical Reacting Engineering", Wiley, New York, NY, 1062.

TABLE 1: ANALYTICAL SOLUTIONS TO THE INTEGRALS IN EQUATIONS 8, 11 AND 14	
$m = 1, S \neq 1$	
$I_d = \frac{1}{3S} \ln(Sx_f^3 + 1 - S) - \frac{1}{6Sk} \ln \left[\left(\frac{k + x_f}{k + 1} \right)^3 (Sx_f^3 + 1 - S) \right] - \frac{1}{3 \cdot 5 S k} \left[\tan^{-1} \left(\frac{2-k}{k-3} \right) - \tan^{-1} \frac{2x_f - k}{k-3} \right]$	
$S = 1, m \neq 1:$	$I_d = -\frac{1}{S} \left[\frac{x_f^{3(1-m)} - 1}{3(1-m)} - \frac{x_f^{2-3m} - 1}{2-3m} \right]$
$S = 1, m = 1:$	$I_d = \ln(x_f) + (1/x_f) - 1$
$S \neq 1:$	
$I_r = \frac{k}{6(1-S)} \ln \left[\left(\frac{k+1}{k+x_f} \right)^3 (Sx_f^3 + 1 - S) \right] - \frac{k}{3 \cdot 5 (1-S)} \left[\tan^{-1} \left(\frac{2x_f - k}{k3 \cdot 5} \right) - \tan^{-1} \left(\frac{2-k}{k3 \cdot 5} \right) \right]$	
$S = 1:$	$I_r = \frac{1}{2x_f^2} - \frac{1}{2}$
$I_g = -\frac{1}{3S} \left[\ln(Sx_f^3 + 1 - S) \right]$	

TABLE 2
PREDICTION OF REACTION TIME AT
A TOTAL PRESSURE OF 1520 kPa

Inlet SO2 ppm	Temp. deg C	BET Area sq m/g	Feed Ratio S	% Gas Absorbed	% Utili- zation	Reaction Time sec
2000	1149	8	2.5	90	36	1.904
1000	1149	8	2.5	80	32	1.880
500	1149	8	2.5	70	28	1.908
2000	1149	15	2.5	90	36	0.541
1000	1149	15	2.5	80	32	0.535
500	1149	15	2.5	70	28	0.543
2000	927	20	2.5	90	36	3.352
1000	927	20	2.5	80	32	3.310
500	927	20	2.5	70	28	3.360
2000	927	30	2.5	90	36	1.490
1000	927	30	2.5	80	32	1.471
500	927	30	2.5	70	28	1.493
2000	927	30	1.0	90	90	17.478
2000	927	30	1.5	90	60	5.033
2000	927	30	2.0	90	45	2.486
2000	927	30	3.0	90	30	0.994

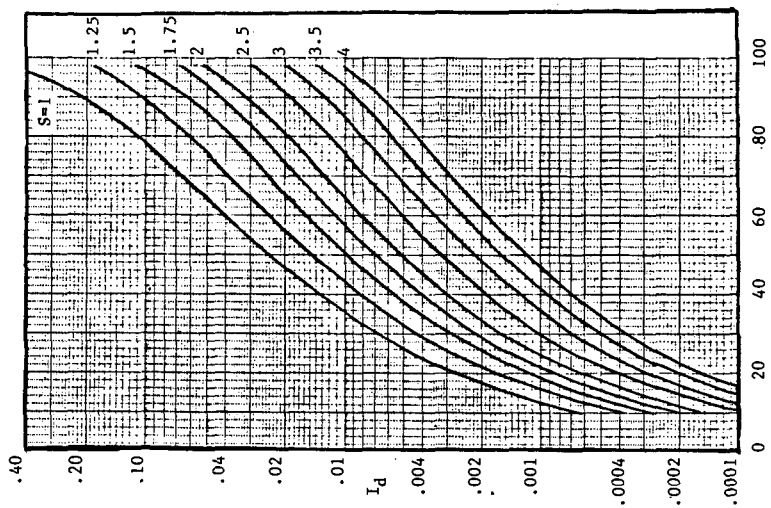


FIGURE 4 VALUES OF I_d FOR $m = 0.62$

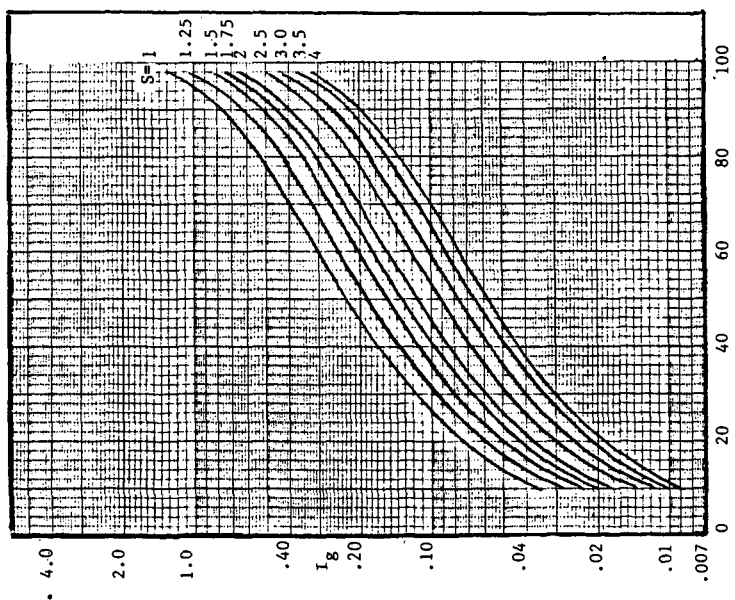


FIGURE 3 VALUES OF I_g

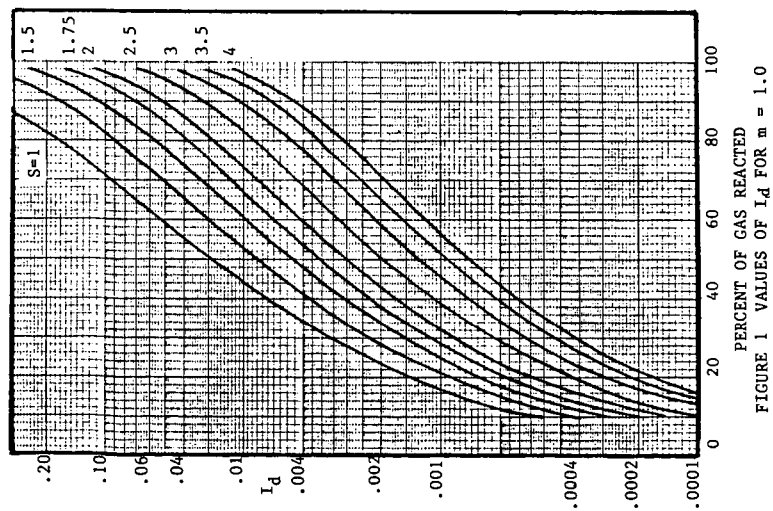


FIGURE 1 VALUES OF I_d FOR $m = 1.0$

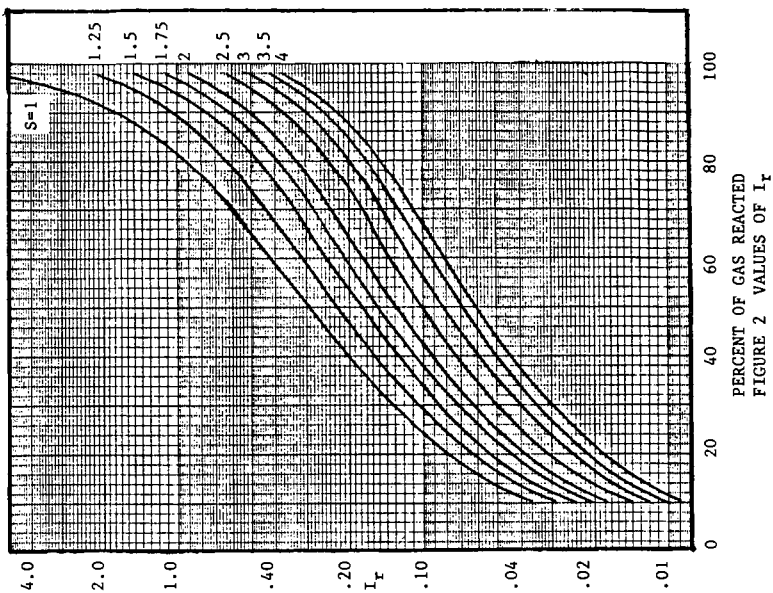


FIGURE 2 VALUES OF I_r